

Supporting Information for:

# A Field-Based Approach for Determining ATOFMS Instrument Sensitivities to Ammonium and Nitrate

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## Dynamic Range Exceedances of the Data Acquisition Board.

Ion signal intensities produced by laser ablation/ionization can vary dramatically from shot-to-shot, due to inhomogeneities in the laser beam [1], and due to differing ionization efficiencies among the chemical species of interest [2]. As a result, laser ablation/ionization of a single particle can produce a very large quantity of ions in a narrow  $m/z$  interval that exceeds the dynamic range of the 8-bit data acquisition board used to digitize the mass spectra collected at Riverside in 1996 and 1997. While conducting the present analysis, a peculiar feature was observed among a small class of particles that yielded ion signals at  $m/z < 3$ , which were large enough to exceed the dynamic range of the data acquisition board. Mass spectra of this type have been reported in ATOFMS data from ambient and emission source testing experiments [3, 4], and are believed to result when ATOFMS instruments encounter certain types of dust-containing particles. The peculiar feature observed in mass spectra of this type is a substantially elevated noise level in the  $0 < m/z < 60$  Dalton range. The elevated noise levels at  $m/z$  18 and 30 make it impossible to estimate the quantities of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  that were initially present in these particles. Therefore,  $\text{Resp}_{\text{NH}_4^+}$  and  $\text{Resp}_{\text{NO}_3^-}$  from particles of this type are assumed to be zero in the present analysis. Only 3.3% of the single-particle spectra analyzed in the present work (802 out of 24502) are affected by this assumption. The affected spectra are believed to result from ablation/ionization of resuspended dust particles, which are hydrophobic and hence unlikely to accumulate significant amounts of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Therefore, disregarding the ion signals at  $m/z$  18 and 30 in this small class of spectra should not have a significant effect on results of the present study. However, when attempting to determine ATOFMS instrument sensitivities to chemical species that are known to be abundant in dust aerosols (e.g. Si, Fe, Al), it may be necessary to estimate and subtract the mass spectrometer noise level from the total mass spectrum generated by ablation/ionization of each particle in this specific class.

When an ion signal exceeds the dynamic range of the 8-bit data acquisition board, the signal height reaches a maximum recordable value of  $2^8$  arbitrary units while the width continues to increase nonlinearly. This hinders our ability to reliably measure the areas of very large ion signals. Fortunately, dynamic range exceedances at  $m/z$  18 and 30 were relatively infrequent among the single-particle spectra analyzed in the present work. Ion signals at  $m/z$  18 and 30 exceeded the

dynamic range in only 763 (3.2%) and 668 (2.8%) of the 23700 spectra, respectively, that were unaffected by the elevated noise levels described above ( $24502 - 802 = 23700$ ). Hence, dynamic range limitations of the data acquisition board should not have a significant effect on the results of the present study.

## Estimation of ATOFMS Particle Detection Efficiencies

In the present work, the procedure for estimating ATOFMS particle detection efficiencies is modified slightly from that described by Allen et al. [5]. In the procedure described by Allen et al., each impactor size interval is subdivided into 10 narrower size intervals,  $j$ . Individual particle spectra acquired by ATOFMS are aggregated into these narrow size intervals based upon their measured aerodynamic diameters. Once aggregated, all particles within a given size interval are assumed to be of identical aerodynamic size,  $\overline{D_{a,j}}$ , calculated as the logarithmic mean of the upper and lower limits of size interval  $j$ . The physical diameter of particles in each size interval,  $\overline{D_{p,j}}$ , is calculated by assuming all particles in size interval  $j$  are spherical with density,  $\rho_p = 1.3 \text{ g cm}^{-3}$ , and aerodynamic diameter,  $D_a = \overline{D_{a,j}}$ . Aggregated ATOFMS data collected during each intensive operating period (IOP) are then compared with impactor measurements collected over the corresponding time period and size interval, using the following model:

$$m_i = \sum_{j \subset i} \frac{N_j \alpha \overline{D_{a,j}}^\beta \frac{\pi}{6} \rho_p \overline{D_{p,j}}^3}{V_i} + \epsilon_i \quad (1)$$

where subscript  $i$  represents the particle ensemble within a specified aerodynamic diameter interval, sampled during a given IOP. In Equation 1,  $m_i$  is the impactor mass concentration measurement of particle ensemble  $i$ ,  $N_j$  is the number of particle spectra recorded by ATOFMS in size interval  $j$ ,  $V_i$  is defined in Equation 3 below, and the parameters  $\alpha$  and  $\beta$  are determined by minimizing the sum of squared residual aerosol mass concentrations,  $\sum_i \epsilon_i^2$ , by nonlinear regression. For brevity, the procedure outlined above uses slightly different notation than that used by Allen et al. [5].

In the present work, the procedure of Allen et al. [5] is modified slightly to eliminate the

aggregation of ATOFMS data into narrow size intervals. The modified regression model is

$$m_i = \sum_{j \subset i} \frac{\alpha D_{a,j}^\beta \frac{\pi}{6} \rho_p D_{p,j}^3}{V_i} + \epsilon_i \quad (2)$$

where the subscript  $j$  now represents an *individual* particle spectrum acquired by ATOFMS, rather than an aggregation of particle spectra in a narrow size interval. In Equation 2,  $D_{a,j}$  is the *single-particle* aerodynamic diameter measured by ATOFMS, rather than an assumed mean aerodynamic diameter, and  $D_{p,j}$  is calculated from  $D_{a,j}$  for each *individual particle*. As in the procedure of Allen et al. [5], all particles are assumed to be spherical with  $\rho_p = 1.3 \text{ g cm}^{-3}$ .

In Equations 1 and 2,  $V_i$  refers to the volume of air sampled by ATOFMS ( $\text{m}^3$ ) during the IOP when particle ensemble  $i$  was sampled. These sample volumes are calculated as

$$V_i = Q_{\text{ATOFMS}} \times (t_{\text{IOP},i} - t_{\text{off},i} - t_{\text{busy},i}) \quad (3)$$

where  $Q_{\text{ATOFMS}}$  is the volumetric flow rate of ambient air through the ATOFMS instrument ( $20 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ ) [6, 7],  $t_{\text{IOP},i}$  is the duration of the IOP (s) when particle ensemble  $i$  was sampled,  $t_{\text{off},i}$  is the amount of time (s) that the ATOFMS instrument was off-line during the IOP, and  $t_{\text{busy},i}$  is the amount of time (s) the ATOFMS electronic data acquisition system was busy recording particle data [5].

To calculate  $t_{\text{off},i}$ , ATOFMS data collected during the given IOP are searched for gaps of 2 minutes or longer when no particle data were recorded. These data gaps are assumed to be periods when the ATOFMS instrument was off-line. The sum of all such data gaps within the IOP when particle ensemble  $i$  was sampled, is designated  $t_{\text{off},i}$ .

The amount of time during each IOP that the ATOFMS electronic data acquisition system was busy recording particle data is calculated by

$$t_{\text{busy},i} = A_1 \times \text{Sized}_i + A_2 \times \text{Hit}_i + A_3 \times (\text{AvgHitPos}_i \times \text{Hit}_i) \quad (4)$$

where  $\text{Sized}_i$  is the number of  $D_a$  measurements that the ATOFMS instrument recorded during the IOP when particle ensemble  $i$  was sampled,  $\text{Hit}_i$  is the number of particle spectra that the ATOFMS

instrument recorded, and  $\text{AvgHitPos}_i$  is the average folder position each particle spectrum was stored in.  $A_1$  is the time required to record a  $D_a$  measurement by the data acquisition system,  $A_2$  is the time required to record a particle spectrum, and  $A_3$  is the amount of additional time required to record each spectrum depending on the number of spectra that are already stored in the given folder. The parameters  $A_1$ ,  $A_2$ , and  $A_3$ , were measured as 130 ms, 504 ms, and 0.167 ms, respectively, for the data acquisition system used at Riverside in 1996, and 100 ms, 450 ms, and 0.244 ms, for the system used at Riverside in 1997.

### Criteria for Evaluating the Significance of an $R^2$ Value.

In the residual analyses described in the present study,  $R^2$  values are discussed only if they exceed a critical value, defined as follows.

$$R^2 > \frac{(t_{df,x})^2}{df + (t_{df,x})^2} \quad (5)$$

where  $R^2$  is the correlation coefficient squared and  $t_{df,x}$  is the critical value associated with Student's  $t$ -distribution at a confidence level of  $1 - 2x$ , given  $df$  degrees of freedom [8]. In the present work, we seek  $R^2$  values which are greater than zero with 95% confidence (i.e.  $x = 0.025$  in Equation 5). The number of degrees of freedom is defined as two less than the number of data points used to calculate  $R^2$ . The critical  $R^2$  values required to satisfy Equation 5 with 95% confidence decrease as the number of data points increases.

In some cases, an  $R^2$  value satisfies Equation 5 with 95% confidence, but removal of a single data point renders the  $R^2$  value statistically insignificant at the 95% confidence level. This indicates that the apparent correlation is largely due to the presence of only one data point, and is not sufficient evidence that the correlation is physically meaningful. Therefore,  $R^2$  values in this regime are not discussed in the present paper.

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